Journal of
Holography and Speckle
Vol. 5, 1–4, 2009

Temperature Dependence of Photorefractive Response of $Sn_2P_2S_6$

A. Shumelyuk[1,*], A. Ruediger[2], O. F. Schirmer[3], B. Hilling[3], V. Dieckmann[3], H. Brüning[3], T. Schemme[3], M. Imlau[3], and S. Odoulov[1]

[1] *Institute of Physics, National Academy of Sciences, 46, Science Avenue, 03 650 Kyiv, Ukraine*
[2] *INRS-EMT, Université du Québec, 1650 Boulevard Lionel-Boulet, Varennes J3X 1S2, Canada*
[3] *Department of Physics, University of Osnabrück, Barbarastr. 7, 49076 Osnabrück, Germany*

The photorefractive response in $Sn_2P_2S_6$ (SPS) is studied as a function of temperature with two-beam coupling experiments. The temperature dependences of the diffusion field and the electrooptic coefficient are the main reasons for the considerable decrease of the gain factor when cooling the sample from ambient temperature down to 150 K. At temperatures below 150 K, light-induced absorption gratings appear that are responsible for beam coupling, and the sign of the gain factor is dependent on the wavelength of the recording light.

Keywords:

1. INTRODUCTION

The photorefraction in nominally undoped Di-tin-hexatiohypodiphosphate ($Sn_2P_2S_6$, SPS) is caused at room temperature by diffusion mediated charge redistribution if red light is used for the recording[1] and by light-induced charge hopping for near infrared recording.[2] The appearing space charge depends, in both cases, on the diffusion field $E_D = (k_B T/e)(2\pi/\Lambda)$, i.e., it is directly proportional to the sample temperature. Here k_B is the Boltzmann constant, e is the electron charge, $\Lambda = \lambda/2\sin(\theta/2)$ is the grating spacing, θ is a full angle between two recording waves in the air, and λ is the light wavelength in vacuum.

The other temperature dependent parameters that affect the photorefractive index change are the electrooptic coefficient r_{eff}, the index of refraction n, and the Debye screening length $\ell_s = \sqrt{\varepsilon\varepsilon_0 k_B T/e^2 N_{eff}}$, with N_{eff} standing for the effective trap density (see, e.g., Ref. [3]). While E_D is obviously decreasing with decreasing temperature, the dependence of the other factors on T may vary for different crystals. In addition, in some materials, like nominally undoped $LiNbO_3$, cooling down may change the dominant type of the charge transport from diffusion at room temperature to photovoltaic at liquid nitrogen temperature[4] with qualitatively different temperature dependence for the developing space charge field. Thus, for any photorefractive crystal it is difficult to predict what kind of temperature dependence it will feature upon cooling without complete knowledge of many different parameters. This is especially true for $Sn_2P_2S_6$ crystals, for which the available information is more limited comparing, e.g., to that about classical photorefractive crystals like $LiNbO_3$ and $BaTiO_3$.

In this paper, we present to our knowledge the first attempt to study low temperature photorefraction in $Sn_2P_2S_6$. Earlier we reported on cooling $Sn_2P_2S_6$ down to −8 °C to eliminate the appearence of the compensation grating.[5] In the present study the measurements are performed within a much wider temperature range. The main tendency observed is the decrease of the gain factor at lower temperatures that can be explained by the reduction of the diffusion field $E_D(T)$ and of the electrooptic coefficient $r(T)$. The small and nearly temperature independent coupling in the sample cooled down to 150 K changes its sign for certain light wavelength. This behavior is attributed to the appearance of amplitude gratings because of nonlinear absorption.

2. EXPERIMENTAL DETAILS

The measurements are performed with nominally undoped (yellow) $Sn_2P_2S_6$ crystals of two different kinds, crystals with a pronounced compensation grating at room temperature (Type 1 crystals) or with one dominating charge species in grating recording (Type 2 crystals).[1]

Several spectral lines of an Ar–Kr ion laser operating at the lowest transverse mode TEM_{00} but with several longitudinal modes are used for photorefractive grating

*Author to whom correspondence should be addressed.

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recording, usually, with the wavelengths 647 nm, 568 nm, and 530.9 nm. For the lowest temperature close to liquid nitrogen temperature the samples become transparent also to the Ar^+ lines 514 nm and 520 nm what allows for using them for grating recording, too. In all cases, care is taken to minimize the path difference of the two interacting waves to less than the coherence length of the laser.

Two unexpanded light beams impinge upon the sample forming a fringe pattern with **K**-vector parallel to the crystal x-axis. The recording waves are usually also polarized parallel to the x-axis, thus involving the largest electrooptic coefficient r_{111} in beam coupling.[1]

In order to cool the sample, a glass Dewar-type vacuum cryostat is used. The inner surface of the glass is not silvered but the walls of the protective wooden box are covered with reflecting metal foil. The cryostat has optical windows aligned along one axis in order to ensure the direct propagation of a light beam through the cold chamber and to allow for the detection of a transmitted beam. The diameter of the cold chamber and the diameter of the windows allowed for tilting the light beam within 15 degrees of arc. This restricted the ultimate space charge field and reduced the beam coupling gain factor but at the same time this allowed for working with low spatial frequencies, for which the space charge limitations are of minor importance. The outer optical windows are heated up to 60 °C to avoid the condensation of natural water vapor from the atmosphere.

The described system ensures the reduction of the sample temperature down to approximately 95 K; then the temperature can be increased gradually by heating a holder with a resistor. The temperature is measured with Ni–Cr thermocouple fixed on the sample holder in close proximity to the sample. The sample heating rate varies within the range of $0.1 \div 2$ K/min; the measurements are done periodically, roughly every 5 minutes. No temperature stabilization is possible. This does not affect, however, the precision of temperature measurement.

The two-beam coupling gain factor

$$\Gamma = \frac{1}{\ell} \ln \frac{I_s}{I_s^0} \qquad (1)$$

is measured in a standard way, with the interaction length ℓ and I_s, I_s^0 standing for the intensities of the transmitted signal beam with and without the pump wave. The intensity of the pump beam is much larger than the intensity of the signal beam, $I_p^0 \gg I_s^0$.

Figure 1 shows the temperature dependences of Γ for the Type 1 sample. The measurements are started for all curves at low temperature, each after 30 min preillumination of the cold sample with a halogen white light lamp.

As one can see, the gain factor strongly decreases with decreasing temperature. Within the error bars of $\pm 15\%$ the gain factor is nearly the same and behaves in a similar way for all three laser wavelengths 647 nm, 568 nm, and 530.9 nm in the temperature range from 340 K down to 150 K. For low temperatures ($T \leq 150$ K) the behavior is qualitatively different: (i) the temperature variations become much weaker and (ii) the value and the sign of the gain factor become obviously wavelength dependent. While for $\lambda = 568$ nm the gain factor tends to zero, it saturates for $\lambda = 647$ nm and 530.9 nm at well defined positive and negative values (squares and dots in Fig. 1, respectively). One more qualitative distinction in gain behavior at low and ambient temperature consists in different spatial frequency dependences of the gain factor. The low temperature gain factor is roughly insensitive to the angle between the recording beams while at ambient temperature a conventional $\Gamma \propto K$ dependence was revealed.

The measurements with Type 2 nominally undoped $Sn_2P_2S_6$ crystals gave similar results except at very low temperatures: no difference in gain factor was observed within the error bars for the three wavelengths within the temperature range from liquid nitrogen to 150 K.

3. DISCUSSION AND SUPPLEMENTARY EXPERIMENTS

For diffusion recording (as also for charge hopping recording) of a photorefractive grating the theoretical expression for the gain factor is as follows (see, e.g., Ref. [3]):

$$\Gamma = \frac{4\pi^2 n^3 r_{\text{eff}} k_B T}{\lambda e \Lambda \cos\theta_0} \cdot \frac{1}{1 + (\sigma_d / \kappa I)} \cdot \frac{1}{1 + K^2 \ell_s^2} \qquad (2)$$

Here r_{eff} is the effective electrooptic constant ($r_{\text{eff}} = r_{111}$ in our case), θ_0 is the half-angle between the recording beams inside the sample, σ_d is the dark conductivity, $K = 2\pi/\Lambda$ is the grating spatial frequency, I is the light intensity, and κ is the specific photoconductivity.

According to Eq. (2) the gain factor contains an explicit linear T-dependence which comes from the expression for the diffusion field. A weaker, but also significant decrease of the gain factor with lowering temperature originates from the temperature dependence of the electrooptic coefficient r_{111}. In close vicinity to the Curie temperature T_c the electrooptic coefficient r_{111} obeys the Curie-Weiss law,[1] $r_{111} \propto 1/\sqrt{T - T_c}$. The larger the difference between the sample temperature and the Curie temperature the stronger becomes the deviation from the Curie-Weiss law and the decrease of the electrooptic coefficient r_{111}.

In principle, also the second and the third factors in Eq. (2) can vary with temperature. It is well known that the specific photoconductivity κ and the dark conductivity σ_d are temperature dependent. However, the light intensity used in our beam coupling experiments ($I \approx 0.2 \div 1$ W/cm^2) was high enough to fulfill the requirement $\sigma_d / \kappa \ll 1$ throughout the whole temperature range where Γ is measured. The deliberate choice of large grating spacings $\Lambda \geq 1$ μm ensured the requirement

$K^2\ell_s^2 \ll 1$ at room temperature. It is valid also throughout the whole temperature range in which Γ is measured because the Debye screening length only decreases when the sample is cooled down.

Qualitatively the measured dependences $\Gamma = \Gamma(T)$ (Fig. 1) are in agreement with the prediction of Eq. (2). The only important discrepancy with the space-charge model appears for the lowest temperatures ($T \leq 150$ K) used in these experiments: neither the inversion of the beam coupling direction (change of gamma sign) nor the independence of the gain factor of the spatial frequency K fit to the model of diffusion mediated space charge formation with one type of movable charge species.

The small value of the gain factor and its independence of the spatial frequency suggest the hypothesis that this gain can be a consequence of amplitude grating recording. The light wave diffracted from the unshifted amplitude grating of nonlinear absorption appears to be either in phase or out of phase with respect to the wave diffracted from the $\pi/2$-shifted phase photorefractive grating, i.e., the gain factors of photorefractive coupling Γ_{pr} and coupling from the absorption grating[7] Γ_{abs} are additive:

$$\Gamma = \Gamma_{pr} + \Gamma_{abs} \tag{3}$$

The coupling factor from the nonlinear absorption grating Γ_{abs} is linearly proportional to the light-induced absorption coefficient $\Delta\alpha$ whereby the proportionality coefficient C depends on the level of the material compensation,[7]

$$\Gamma_{abs} = -C\Delta\alpha \tag{4}$$

Depending on the type of the nonlinear changes of absorption (bleaching or darkening) an additional gain factor changes its sign being positive or negative, respectively.

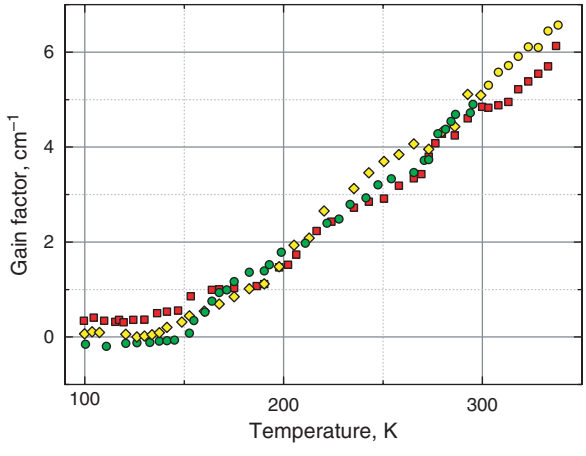

Fig. 1. Temperature dependence of two-beam coupling gain in nominally undoped Type 1 SPS crystal measured with different Kr^+-laser wavelengths, 647 nm (squares), 568 nm (diamonds) 530.9 nm (dots). The total intensities of the recording beams are 0.9 W/cm,^{2} 0.45 W/cm,^{2} and 0.25 W/cm,^{2} respectively, the beam ratio is 1:100, and the fringe spacings are 4.1 μm, 3.6 μm, and 3.4 μm, respectively.

The contribution of a nonlinear absorption grating to two-beam coupling is known for the photorefractive semiconductors GaAs.[7,8] The gain factors in GaAs are rather moderate so that relative changes of coupling because of additional amplitude gratings are very pronounced.

The light-induced variations of the absorption in nominally undoped SPS have been reported earlier both at ambient and at liquid helium temperatures.[9,10] Therefore, it is reasonable to expect a similar behavior also for intermediate temperatures slightly above liquid nitrogen temperature. Indirect support of this statement comes from measurements of the temperature dependences of differential absorption[10] for the nominally undoped Type 1 SPS sample K3. A pseudo-color plot shown in Figure 2 represents the variation of absorption of a sample that has been illuminated with white light at liquid helium temperature and is then gradually heated to ambient temperature. Individual colors mark the difference of the absorption coefficient at any temperature given in abscissa and that measured at liquid helium temperature.

The pronounced changes in absorption, indicated in Figure 2, begin around $T \approx 100$ K. This means that just at that temperature the thermally excited carriers repopulate the energy states of intrinsic defects thus leading to sample darkening at energies about $E_{ph} \approx 2.3$ eV and bleaching at $E_{ph} \leq 1.9$ eV. Naturally, the thermally excited carriers are re-trapped to more deep energy levels. It is reasonable to suppose that photoexcited free carriers, thermalized to a quasiequilibrium state, will be re-trapped in a similar way, thus increasing the population of more deep levels. In other words, we can expect light-induced bleaching for photon energies $E_{ph} \leq 1.9$ eV and, on the opposite, light-induced darkening for $E_{ph} \approx 2.3$ eV. It can be seen from Figure 2 that at $T \approx 100$ K relatively small changes in absorption occur for the photon energy $E_{ph} \approx 2.2$ eV. The light-induced changes in absorption can not be the same as

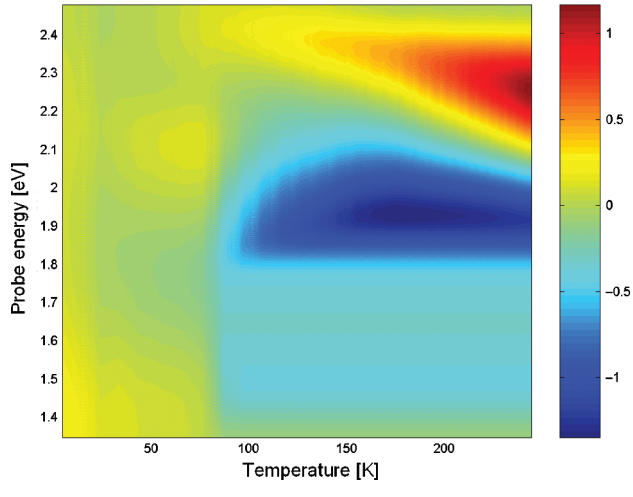

Fig. 2. Temperature dependence of differential absorption. The vertical bar on the right gives color encoding of absorption changes in cm^{-1} with respect to the low reference temperature ≪50 K.

temperature-induced modifications of absorption shown in Figure 2; we believe however that the spectra of $\Delta\alpha(h\nu)$ are qualitatively similar for the two processes.

From the above assumptions a few important qualitative conclusions can be formulated. First, with positive $\Delta\alpha$ at $\lambda = 530.9$ nm one can expect a negative coupling factor Γ_{abs} while for $\lambda = 647$ nm it should be positive. This is exactly what is observed experimentally (see Fig. 1). Second, the absolute value of the positive gain at $\lambda = 647$ nm should be larger than the negative one at $\lambda = 530.9$ nm. This is also in qualitative agreement with the experimental data (Fig. 1).

It should be noted that these effects are present only in nominally undoped Type 1 SPS samples; in Type 2 samples the gain factor measured at all three wavelengths decreases but never changes its sign. We hence can suggest that the light-induced absorption at about 100 K either does not exist or is much smaller than in Type 1 samples. This is in line with other known properties of Type 2 nominally undoped $Sn_2P_2S_6$: they do not manifest, e.g., the increased sensitivity to 1064 nm recording after pre-illumination to white light.[1,2]

4. CONCLUSIONS

Our experiments show that two-beam coupling is SPS becomes less effective when cooling down the samples to liquid nitrogen temperature. The gain factor decreases by more than one order of magnitude from ambient temperature to 100 K. It is shown that the sign of the small residual beam coupling observed in Type 1 nominally undoped SPS at $\approx$ 100 K depends on the wavelength of the recording light. Such a coupling is attributed to the selfdiffraction from the nonlinear absorption grating. This conclusion is supported by the observation of strong thermally-induced variations in the absorption spectrum of SPS pre-illuminated with white light at liquid helium temperature.

Acknowledgments: The financial support of DFG (GRA 695 and IM 37/5-1) is gratefully acknowledged. We are grateful to A. Grabar and I. Stoyka for SPS samples. (A. Shumelyuk and S. Odoulov thank colleagues from Osnabrück university for their kind hospitality.)

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Received: 30 October 2009. Accepted: 2 November 2009.